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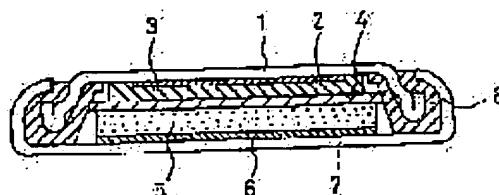
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(54) NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY AND MANUFACTURE OF ACTIVE MATERIAL USED THEREFOR

(57)Abstract:

PURPOSE: To provide a battery having satisfactory charge/discharge characteristic and a long cycle life by using, as an electrode active material, a thermally treated material of an organic Si compound having one or more coupling parts of Si having an organic group and O or a one having Li stored therein.

CONSTITUTION: An organosiloxane such as Si oil which is a polymer consisting of a main chain in which Si having an organic group and O are alternately bonded to each other is used. This compound is treated at 200-600°C in the atmosphere or at 300-1000°C in vacuum or inert atmosphere. The optimum temperature is differed depending on starting materials. The thermally treated material or a mixing agent of the thermally treated material with 8 conductive agent and a binder is molded to form one electrode, and 8 current is carried thereto with a Li-contained material as a counter electrode to store Li ions. As an



electrolyte, a solution 10 which LiClO_4 is dissolved in γ -butyrolactone is use. This electrode can stably store and release Li ions within the range of 0-3V to the metal Li in nonaqueous electrolyte, and used as the negative electrode and/or positive electrode of a secondary battery.

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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by using what carried out occlusion of the lithium to the heat treatment object or said heat treatment object of the organic silicon compound which has at least one or more binding sites of the silicon which has an organic radical, and oxygen as an active material of the electrode of a negative electrode and/or a positive electrode in the nonaqueous electrolyte rechargeable battery which consists of a negative electrode, a positive electrode, and the nonaqueous electrolyte of lithium ion conductivity at least.

[Claim 2] The manufacture approach of of the negative-electrode active material for nonaqueous electrolyte rechargeable batteries according to claim 1 and/or positive active material which are characterized by heat-treating said organic silicon compound in a 200 to 1000 degrees C temperature requirement.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention uses as a negative-electrode active material and/or positive active material the matter which can occlusion emit a lithium or a lithium, and relates to the new negative-electrode active material and the positive active material which repeat charge and discharge were possible for, and were excellent in high capacity and a overcharge overdischarge property about the nonaqueous electrolyte rechargeable battery using the nonaqueous electrolyte of lithium ion conductivity.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte cells using a lithium as a negative-electrode active material are a high voltage and a high energy consistency, and are already widely used as power sources the object for memory-backup, for cameras, etc. as a primary cell with an advantage, like self-discharge is small excellent in dependability over a long period of time. However, with remarkable development of the electronic equipment of a pocket mold, communication equipment, etc., the device which requires a high current output from the cell as a power source appears variously, from a viewpoint of the formation of small lightweight of economical efficiency and a device, re-charge and discharge are possible, and the rechargeable battery of a high energy consistency is demanded strongly in recent years. For this reason, although the researches and developments which advance rechargeable battery-ization of said nonaqueous electrolyte cell which has a high energy consistency are done actively and put in practical use in part, energy density, a charge-and-discharge cycle life, dependability, etc. are still inadequate.

[0003] Conventionally, as positive active material which constitutes the positive electrode of this kind of rechargeable battery, it depends on the gestalt of a charge-and-discharge reaction, and the thing of three sorts of following types is found out. The 1st type is types which only a lithium ion (cation) depends on an intercalation, a day intercalation reaction, etc., and go in and out between the layers of a crystal, and between a grid location or an interstice, such as a metal chalcogen ghost of TiS_2 , MoS_2 , and NbSe_3 grade, and a metallic oxide of MnO_2 , MoO_3 , V_2O_5 , LiXCoO_2 and LiXNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ grade, like **. The 2nd type is a type like conductive polymers, such as the poly aniline, polypyrrole, and poly para-phenylene, with which only an anion mainly depends and frequents stability at a dope and a dedope reaction. The 3rd type is types (an intercalation, a day intercalation or a dope, dedope, etc.) with which both lithium cations and anions like **, such as conductive polymers, such as intercalated graphite and the poly acene, can go in and out.

[0004] As a negative-electrode active material which, on the other hand, constitutes the negative electrode of this kind of cell, although the output voltage as a cell which the case where a metal lithium was used independently combined with the positive electrode using the above positive active material since electrode potential was ** most was the highest and the energy density was also highly desirable, in connection with charge and discharge, the dendrite and the non-**** compound generated on the negative electrode, degradation by charge and discharge was large, and there was a problem that a cycle

life was short. In order to solve this problem, as a negative electrode The alloy of (1) lithium and other metals, such as aluminum, Zn, Sn, Pb, Bi, and Cd, (2) WO₂, MoO₂, Fe₂O₃, the inorganic compound and graphite of TiS₂ grade, The intercalation compound which carried out occlusion of the lithium ion into crystal structures of **, such as a carbonaceous ingredient which calcinates the organic substance and is obtained, or an insertion compound, (3) Using the matter which can occlusion emit the lithium ion of **, such as conductive polymers which doped the lithium ion, such as the poly acene and polyacethylene, is proposed.

[0005]

[Problem(s) to be Solved by the Invention] However, generally, since the electrode potential of these matter is ** from the electrode potential of a metal lithium when a cell is constituted combining the negative electrode using the matter which can occlusion emit lithium ions other than the above metal lithiums as a negative-electrode active material, and the positive electrode using the above positive active material, there is a fault of falling considerably from the case where the operating potential of a cell uses a metal lithium independently as a negative-electrode active material. For example, in using a lithium and alloys, such as aluminum, Zn, Pb, Sn, Bi, and Cd, at 0.2-0.8V, and a carbon-lithium intercalation compound, 0.5 - 1.5V operating potential falls with the lithium ion insertion compound of 0-1V, MoO₂, or WO₂ grade.

[0006] Furthermore, since elements other than a lithium also turn into a negative-electrode component, the capacity and energy density per volume and per weight fall remarkably. For this reason, a charge-and-discharge property is excellent, and in order to obtain the rechargeable battery of the high voltage and a high energy consistency, the negative-electrode active material with a large amount with which the electrode potential to a lithium can carry out occlusion emission of the lithium ion low (it is ****) and reversibly is required [a cycle life is long, and].

[0007] On the other hand, in the above-mentioned positive active material, the 1st type has overcharge and the fault that degradation by collapse of a crystal, generation of the irreversible matter, etc. is large if overdischarge is carried out, although energy density is generally large. Moreover, by the 2nd and 3rd type, there is a fault that capacity and energy density are conversely small.

[0008] For this reason, in order a overcharge property and an overdischarge property are excellent and to obtain the rechargeable battery of high capacity and a high energy consistency, the larger positive active material of the amount which can carry out occlusion emission of the lithium ion reversibly [there are no collapse of a crystal and generation of the irreversible matter which depend on overcharge overdischarge, and] is required.

[0009]

[Means for Solving the Problem] This invention raises using the new matter which consists of what carried out occlusion of the lithium to the heat treatment object or this heat treatment object of an organic silicon compound which has at least one or more bonding sites of the silicon which has an organic radical, and oxygen as an active material of the negative electrode of this kind of cell, and/or the electrode of a positive electrode and which can be lithium ion occlusion emitted in order to solve the above troubles.

[0010] The heat treatment object of the organic silicon compound used as an active material of the negative electrode of this invention cell and/or a positive electrode can be manufactured as follows. What is necessary is just the compound which has at least one or more binding sites of the silicon which has an organic radical as a side chain, and oxygen as an organic silicon compound of a raw material. The silicone oil which is the polymer which consists of a principal chain which silicon and oxygen with an organic radical joined together by turns, and was able to do them especially, silicone rubber or silicone resin, etc. is desirable. These compounds are named generically and called polyorganosiloxane. The part combined with carbon or all hydrogen may be permuted by halogen atoms, such as chlorine, a bromine, and iodine, by the organic radical combined with silicon that what is necessary is just to be by the hydrocarbon group, the alkoxy group, the ammonium shown by -N-R one R₂ (R₁ and R₂ are an alkyl group, an allyl group, a phenyl group, hydrogen, etc.). As an organic radical, a methyl group (-CH₃), an ethyl group (-C₂H₅), a phenyl group (-C₆H₅), a methoxy group (-OCH₃), an ethoxy radical (-OC₂H₅),

etc. are desirable especially.

[0011] By heat-treating these organic silicon compounds at the suitable temperature of the range of 200-1000 degrees C, a condensation polymerization reaction or decomposition breaks out partially, and the compound of the three-dimension network structure generates. In heat treatment to the case of heat treatment in atmospheric air in 200 degrees C - 600 degrees C, a vacuum, or an inert atmosphere, 300 degrees C - 1000 degrees C are especially desirable. The optimal heat treatment temperature changes with differences in the rate contained in the molecular weight of a raw material compound, and a molecular structure part in the raw material molecule of elements, such as a bridge formation condition or silicon, carbon, and oxygen, etc.

[0012] Moreover, occlusion of the lithium to this heat treatment object can be performed as follows. namely, mixing with (1) this heat treatment object or this heat treatment object, an electric conduction agent, a binder, etc. -- what fabricated the mixture in the predetermined configuration being used as one electrode (operation pole), and the matter containing lithium metal or a lithium as another electrode (counter electrode) The approach of making two electrodes counter in contact with the nonaqueous electrolyte of lithium ion conductivity, constituting an electrolysis cell, energizing with the suitable current for the direction in which an operation pole carries out a cathode reaction, and carrying out occlusion of the lithium ion electrochemically.

[0013] (2) mixing with this heat treatment object or this heat treatment object, an electric conduction agent, a binder, etc. -- fabricate a mixture in a predetermined configuration and include in a cell by using as an electrode what the alloy of lithium metal or a lithium etc. was stuck by pressure or contacted to this, and used it as the laminating electrode at it. The approach by which self-discharge is carried out and occlusion of the lithium is electrochemically carried out when this laminating electrode touches an electrolyte within a cell.

[0014] (3) Use this heat treatment object as the active material of one electrode, contain a lithium in another electrode and constitute the cell using the active material which can occlusion emit a lithium ion. The approach by which occlusion of the lithium is carried out to this heat treatment object by performing charge and discharge while in use as a cell. Thus, what carried out occlusion of the lithium to the heat treatment object or this heat treatment object obtained is used as an active material of a negative electrode and/or a positive electrode.

[0015] The electrode which uses as an active material what carried out occlusion of the lithium to the heat treatment object or this heat treatment object of an organic silicon compound which depends on this invention uses this for positive/negative two poles, and it can constitute a rechargeable battery and it can also be used for it combining the electrode using various kinds of negative-electrode active materials or positive active material of other which can occlusion emit an above-mentioned lithium or an above-mentioned lithium ion as another electrode, using this as an electrode of either a positive electrode or a negative electrode. Especially the electrode that uses as an active material what carried out occlusion of the lithium to the heat treatment object or this heat treatment object of an organic silicon compound of this invention The electrode potential to a metal lithium from the charge-and-discharge capacity of the **** field not more than 1 V being large Using this as a negative electrode, when the electrode potential to a metal lithium like **, such as the above-mentioned metallic-oxide metallurgy group chalcogen ghost, combines with the positive electrode using the active material of high potential beyond 2V, are a high-voltage high energy consistency, and it excels in a high current charge-and-discharge property. Since the small rechargeable battery of degradation by overcharge overdischarge is obtained, it is especially desirable.

[0016] On the other hand as an electrolyte, gamma-butyrolactone, propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, 1, 2-dimethoxyethane, a tetrahydrofuran, Independent or the organic electrolytic solution which dissolved the lithium ion dissociative salt of LiClO₄, LiPF₆, LiBF₄, and LiCF₃SO₃ grade in the mixed solvent as a supporting electrolyte of organic solvents, such as dioxolane and dimethyl formamide, What is necessary is just nonaqueous electrolyte of lithium ion conductivity, such as inorganic solid electrolytes, such as a giant-molecule solid electrolyte which made said lithium salt dissolve to giant molecules, such as

polyethylene oxide and the poly FOSUFAZEN bridge formation object, or Li_3N , and LiI .

[0017]

[Function] Occlusion emission of the lithium ion can be repeatedly carried out [in the inside of nonaqueous electrolyte] to stability to a metal lithium in the range of the electrode potential of 0-3V at least (an intercalation, a day intercalation or a dope, dedope, etc.), and it can be repeatedly used for the electrode which uses as an active material what carried out occlusion of the lithium to the heat treatment object or this heat treatment object of an organic silicon compound of this invention as the negative electrode and/or positive electrode of the rechargeable battery in which charge and discharge are possible according to such electrode reaction. It has the high capacity field which carries out occlusion emission and can carry out the repeat charge and discharge of the lithium ion to stability in the **** potential field of 0-1V especially to a lithium criteria pole (lithium metal).

[0018] Moreover, greatly [it is remarkable, the amount, i.e., the charge and discharge capacity, which can carry out occlusion emission of the lithium ion reversibly compared with carbonaceous ingredients, such as graphite conventionally used as an electrode of this kind of cell, and], since polarization of charge and discharge is small, the charge and discharge in a high current are possible, degradation which considers decomposition by overcharge overdischarge etc. as a cause further can hardly be seen, but it is very stable and the long cell of a cycle life can be obtained.

[0019] Thus, although the reason the outstanding charge-and-discharge property is acquired is not necessarily clear, the heat treatment object of the organic silicon compound which is a new active material by this invention is a high molecular compound of the network structure which uses association of silicon and oxygen as a principal chain, or the three-dimension network structure, its mobility of the lithium ion in the inside of this structure is high, and since there are very many sites which can carry out occlusion of the lithium ion, it is presumed because occlusion emission of a lithium ion is easy.

[0020]

[Example] Below, the example of this invention is explained based on drawing. Drawing 1 is the sectional view of the coin mold cell in which an example of the test cell used for the performance evaluation of the electrode active material of the nonaqueous electrolyte rechargeable battery which depends on this invention is shown.

[0021] In drawing 1, 1 is a counter electrode case which serves as a counter electrode terminal, and carries out spinning of the plate made from stainless steel which carried out nickel plating of outside one side. 2 is a counter electrode charge collector which consists of the network made from stainless steel, and spot welding is carried out to the counter electrode case 1. A counter electrode 3 pierces a given thickness Mino aluminum plate in diameter of 15mm, fixes to the counter electrode charge collector 2, and sticks by pressure what pierced the given thickness Mino lithium foil in diameter of 14mm on it. 7 is the operation pole case made from stainless steel which carried out nickel plating of outside one side, and serves as the operation pole terminal.

[0022] 5 is the operation pole constituted using the comparison active material which depends on the active material which depends on below-mentioned this invention, or a conventional method, and pressing is carried out to the operation pole charge collector 6 and one which consist of a network made from stainless steel. 4 is a separator which consists of a porosity film of polypropylene, and the electrolytic solution sinks in. an operation pole case opening edge bends it inside at the same time 8 is a gasket which makes polypropylene a subject, intervenes between the counter electrode case 1 and the operation pole case 7 and maintains the electric insulation between a counter electrode and an operation pole -- having -- caulking **** -- therefore, cell contents are sealed and closed to things. The electrolyte used what dissolved one mol /of lithium perchlorates LiClO_4 in propylene carbonate and 1 and volume ratio of 2-dimethoxyethane 1:1 mixed solvent. The magnitude of a cell was 1.6mm in the outer diameter of 20mm, and thickness.

[0023] The example of production of an active material is shown below.

(Example 1 of production) The operation pole 5 was produced as follows. In order to volatilize a solvent by 100-degreeC in atmospheric air for 10 hours, stoving of the solution (Toshiba Silicone silicon varnish TSR 117) which diluted with the xylene the poly methylphenyl siloxane (PMPS) which is an organic

silicon compound was carried out. Next, this dry matter was heat-treated at 200 degrees C among atmospheric air for 5 hours. The grinding particle size regulation was carried out to the particle size of 53 micrometers or less after cooling. The obtained heat treatment object is used as the active material 1 which depends on this invention. As an electric conduction agent to this graphite It considers as a mixture. as a binder -- bridge formation mold acrylic acid resin etc. -- the weight ratio 30:65:5 -- comparatively -- coming out -- mixing -- an operation pole -- next, this operation pole -- after carrying out pressing of the mixture to a with a diameter thickness [0.5mm thickness of 15mm] pellet by 2 ton/cm² with the operation pole charge collector 6 which consists of a network made from stainless steel, what carried out heating under reduced pressure desiccation at 100 degrees C for 10 hours was made into the operation pole. It considered as the cell of the above-mentioned configuration using this operation pole.

[0024] Thus, after neglect aging of the produced cell was carried out for one week at the room temperature, the below-mentioned charge and discharge test was performed. Since alloying advanced enough and the lithium foil served as a Li-aluminum alloy altogether substantially according to this aging when the lithium-aluminum laminating electrode of a counter electrode touches nonaqueous electrolyte within a cell, cell voltage became the value which fell by about 0.4v compared with the case where a metal lithium is independently used as a counter electrode, and was stabilized.

[0025] A discharge property was shown in drawing 2 and drawing 3 and the cycle property of one to 5 cycle were shown in drawing 4 for the charge property of the 3 cycle eye when performing the cell produced as mentioned above by 0.4mA constant current, and performing a charge-and-discharge cycle on condition that termination electrical-potential-difference-0.4V of charge (the direction of a current which carries out the cell reaction by which occlusion of the lithium ion is carried out to an operation pole), and termination electrical-potential-difference 2.5V of discharge (the direction of a current which carries out the cell reaction to which a lithium ion is emitted from an operation pole). Moreover, the discharge property was shown in drawing 6 and the cycle property of one to 5 cycle was shown for the charge property of 3 cycle eye in the electrical-potential-difference range of -0.8V-2.5V in drawing 5 at drawing 7 . In addition, the charge-and-discharge cycle was started from charge.

[0026] (Example 2 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 10 hours at 300 degrees C among atmospheric air, the active material 2 was produced by the same approach as the example 1 of production, and the same cell was produced. the same approach as the example 1 of production -- measurement of a charge-and-discharge property -- carrying out -- the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V -- drawing 2 R> 2, drawing 3 , and drawing 4 -- moreover, the discharge property was shown in drawing 6 and the cycle property was shown for the charge property in the electrical-potential-difference range of -0.8V-2.5V in drawing 5 at drawing 7 .

[0027] (Example 3 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 10 hours at 400 degrees C among atmospheric air, the active material 3 was produced by the same approach as the example 1 of production, and the same cell was produced. The charge-and-discharge property was measured by the same approach as the example 1 of production, the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V was shown in drawing 2 R> 2, drawing 3 , and drawing 4 , and the charge-and-discharge property in the electrical-potential-difference range of -0.8V-2.5V was shown in drawing 5 , drawing 6 , and drawing 7 . - the generation of gas there are also no signs that the lithium deposits to the operation pole side when decomposition observation of each cell of a charge condition and a discharge condition is carried out for the charge and discharge of 0.8V-2.5V after 10 cycle ***** , and according to electrolytic disassembly etc. -- a pole -- it is little and it was checked that the charge-and-discharge reaction of an operation pole is occlusion emission of the lithium ion to an active material substantially.

[0028] (Example 4 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 10 hours at 500 degrees C among atmospheric air, the active material 4 was produced by the same approach as the example 1 of production, and the same cell was produced. The charge-and-discharge property was measured by the same approach as the example 1 of production, the charge-and-

discharge property in the electrical-potential-difference range of -0.4V-2.5V was shown in drawing 2 R> 2, drawing 3 , and drawing 4 , and the charge-and-discharge property in the electrical-potential-difference range of -0.8V-2.5V was shown in drawing 5 , drawing 6 , and drawing 7 .

[0029] (Example 5 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 10 hours at 600 degrees C among atmospheric air, the active material 5 was produced by the same approach as the example 1 of production, and the same cell was produced. The charge-and-discharge property was measured by the same approach as the example 1 of production, the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V was shown in drawing 2 R> 2, drawing 3 , and drawing 4 , and the charge-and-discharge property in the electrical-potential-difference range of -0.8V-2.5V was shown in drawing 5 , drawing 6 , and drawing 7 .

[0030] (Example 6 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 5 hours at 500 degrees C among nitrogen-gas-atmosphere mind, the active material 6 was produced by the same approach as the example 1 of production, and the same cell was produced. By the same approach as the example 1 of production, the charge-and-discharge property of -0.4V-2.5V was measured, the discharge property was shown in drawing 9 and the cycle property was shown for the charge property in drawing 10 at drawing 8 .

[0031] (Example 7 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 5 hours at 700 degrees C among nitrogen-gas-atmosphere mind, the active material 7 was produced by the same approach as the example 1 of production, and the same cell was produced. By the same approach as the example 1 of production, the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V was measured, and the result was shown in drawing 8 R> 8, drawing 9 , and drawing 10 .

[0032] (Example 8 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 12 hours at 800 degrees C among nitrogen-gas-atmosphere mind, the active material 8 was produced by the same approach as the example 1 of production, and the same cell was produced. The charge-and-discharge property was measured by the same approach as the example 1 of production, and the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V was shown in drawing 8 , drawing 9 , and drawing 10 . Moreover, the discharge property was shown in drawing 12 and the cycle property was shown for the charge property in the electrical-potential-difference range of -0.8V-2.5V in drawing 11 at drawing 13 .

[0033] (Example 9 of production) Except having made heat treatment of the above-mentioned PMPS dry matter into 12 hours at 1000 degrees C among nitrogen-gas-atmosphere mind, the active material 9 was produced by the same approach as the example 1 of production, and the same cell was produced. The charge-and-discharge property was measured by the same approach as the example 1 of production, the charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V was shown in drawing 8 , drawing 9 , and drawing 10 , and the charge-and-discharge property in the electrical-potential-difference range of -0.8V-2.5V was shown in drawing 11 , drawing 12 , and drawing 13 .

[0034] (Example 1 of a comparison) For the comparison, the cell was produced by the same approach as the example 1 of production instead of the active material 1 in the example 1 of production except having used the same graphite as the graphite used as an electric conduction agent as an active material. The charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V is measured like the example 1 of production, and the result is shown in drawing 2 , drawing 3 , and drawing 4 .

[0035] (Example 2 of a comparison) The cell was produced by the same approach as the example 1 of production except having used the silicon dioxide SiO₂ as an active material instead of the active material 1 in the example 1 of production for the comparison. The charge-and-discharge property in the electrical-potential-difference range of -0.4V-2.5V is measured like the example 1 of production, and the result is shown in drawing 2 , drawing 3 , and drawing 4 R> 4.

[0036] The cell using the heat treatment object of the organic silicon compound by this invention as an active material all has a remarkably large charge-and-discharge capacity compared with the examples 1 and 2 of a comparison, and it turns out that the reversible field of charge and discharge is expanded

remarkably so that clearly from drawing 2 -13. Moreover, the fall (cycle degradation) of the discharge capacity by the repeat of charge and discharge is remarkably small. Furthermore, it crosses to all charge-and-discharge fields, the difference of the operating potential of charge and discharge is remarkably small, and it turns out that polarization (internal resistance) of a cell is remarkably small, and high current charge and discharge are easy. In the heat treatment object of the organic silicon compound which is the active material of the operation pole of the cell which depends on this invention as mentioned above, silicon, oxygen, and carbon live together, and by having the network structure or the three-dimension network structure which those atoms combined with direct [both], this has the high mobility of a lithium ion, and is presumed because there are many sites which can carry out occlusion of the lithium ion.

[0037] The cell using the active material which depends on this invention receives a Li-aluminum alloy electrode. Moreover, like the electropositive potential field of 1.0-2.5V (it corresponds to Abbreviation 1.4-2.9V to a metal lithium) Or more than it, since the charge-and-discharge capacity of the **** potential field of -0.4-+0.6V (it corresponds to Abbreviation 0-1V to a metal lithium) is large, it is not only used as positive active material of a nonaqueous electrolyte rechargeable battery, but it turns out that it excels also as a negative-electrode active material. More greatly, the charge-and-discharge capacity in a **** potential field has more **** potential, and is more excellent in the cell using the active materials 1, 2, 3, 6, and 7 which heat-treated below 700 degrees C among 200 degrees C - 400 degrees C and an inert atmosphere especially among atmospheric air as a negative-electrode active material.

[0038] In addition, in an example, although only the case of a lithium-aluminium alloy was shown as a counter electrode This invention is not limited to an example. As mentioned above The alloy of a metal lithium, a lithium, and other metals, such as Zn, Sn, Pb, and Bi, The negative electrode which uses as an active material the matter which can occlusion emit the lithium of **, such as a conductive polymer in which a dope of lithium ions, such as carbon, a lithium insertion compound of MoO₂, WO₂, and Fe₂O₃ grade, polyacetylene, polypyrrole, and the poly acene, is possible, The metallic oxide of TiS₂, MoS₂, the metal chalcogen ghost of NbSe₃ grade, MnO₂ and MoO₃, V₂O₅, LiXCoO₂ and LiXNiO₂, and Li_xMn₂O₄ grade, Conductive polymers, such as the poly aniline, polypyrrole, poly para-phenylene, and the poly acene, It cannot be overemphasized that the positive electrode which uses as an active material the matter which can occlusion emit the lithium cation and/or anion like **, such as intercalated graphite, can be used combining the electrode which considers as a counter electrode and depends on this invention.

[0039]

[Effect of the Invention] This invention as mentioned above, as an active material of the negative electrode of a nonaqueous electrolyte rechargeable battery, and/or the electrode of a positive electrode The new active material which consists of what carried out occlusion of the lithium to the heat treatment object or this heat treatment object of an organic silicon compound which has at least one or more bonding sites of the silicon which has an organic radical, and oxygen is used. Since [remarkable, the amount, i.e., the charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly by charge and discharge, / large and] polarization of charge and discharge is small, The charge and discharge in a high current are possible, degradation of decomposition, crystal collapse, etc. by overcharge overdischarge is hardly seen further, but it is very stable and the long cell of a cycle life can be obtained. Moreover, when this active material by this invention is especially used as a negative-electrode active material, it has the ***** effectiveness -- the cell of the high voltage and a high energy consistency can be obtained.

[Translation done.]

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ABSTRACT:

PURPOSE: To provide a battery having satisfactory charge/discharge characteristic and a long cycle life by using, as an electrode active material, a thermally treated material of an organic Si compound having one or more coupling parts of Si having an organic group and O or a one having Li stored therein.

CONSTITUTION: An organosiloxane such as Si oil which is a polymer consisting of a main chain in which Si having an organic group and O are alternately bonded to each other is used. This compound is treated at 200-600°C in the atmosphere or at 300-1000°C in vacuum or inert atmosphere. The optimum temperature is differed depending on starting materials. The thermally treated material or a mixing agent of the thermally treated material with 8 conductive agent and a binder is molded to form one electrode, and 8 current is carried thereto with a Li-contained material as a counter electrode to store Li ions. As an electrolyte, a solution 10 which LiClO<SB>4</SB> is dissolved in γ-butyrolactone is use. This electrode can stably store and release Li ions within the range of 0-3V to the metal Li in nonaqueous electrolyte, and used as the negative electrode and/or positive electrode of a secondary battery.

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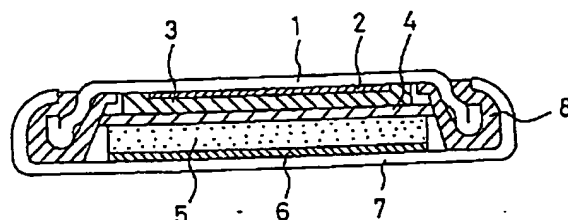
(54)【発明の名称】 非水電解質二次電池及びそれに用いる活物質の製造方法

(57)【要約】

【目的】 充放電特性が優れ、かつサイクル寿命の長い新規な非水電解質二次電池及びその電極の活物質の製造方法。

【構成】 負極と正極とリチウムイオン導電性の非水電解質とから少なくとも成る非水電解質二次電池において、負極及び／又は正極の電極の活物質として、有機基を有するケイ素と酸素の結合部位を少なくとも1つ以上有する有機ケイ素化合物を200℃～1000℃で熱処理した化合物または該熱処理物にリチウムを吸蔵させたものを用いる。

【効果】 充放電容量が大きく高エネルギー密度であり、かつ充放電時の分極(内部抵抗)が小さいため大電流充放電が容易であると同時に、過充電過放電による劣化が小さく、サイクル寿命が長い。。



【特許請求の範囲】

【請求項1】 負極と正極とリチウムイオン導電性の非水電解質とから少なくとも成る非水電解質二次電池において、負極及び／又は正極の電極の活物質として、有機基を有するケイ素と酸素の結合部位を少なくとも1つ以上有する有機ケイ素化合物の熱処理物又は前記熱処理物にリチウムを吸蔵させたものを用いたことを特徴とする非水電解質二次電池。

【請求項2】 前記有機ケイ素化合物を200℃から1000℃の温度範囲で熱処理する事の特徴とする請求項1記載の非水電解質二次電池用の負極活物質及び／又は正極活物質の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、リチウムもしくはリチウムを吸蔵放出可能な物質を負極活物質及び／又は正極活物質とし、リチウムイオン導電性の非水電解質を用いる非水電解質二次電池に関するものであり、繰返し充放電が可能で、高容量かつ過充電過放電特性の優れた、新規な負極活物質及び正極活物質に関するものである。

【0002】

【従来の技術】負極活物質としてリチウムを用いる非水電解質電池は、高電圧、高エネルギー密度で、かつ自己放電が小さく長期信頼性に優れる等の利点により、一次電池としてはメモリーバックアップ用、カメラ用等の電源として既に広く用いられている。しかしながら、近年携帯型の電子機器、通信機器等の著しい発展に伴い、電源としての電池に対し大電流出力を要求する機器が多種多様に出現し、経済性と機器の小型軽量化の観点から、再充放電可能で、かつ高エネルギー密度の二次電池が強く要望されている。このため、高エネルギー密度を有する前記非水電解質電池の二次電池化を進める研究開発が活発に行われ、一部実用化されているが、エネルギー密度、充放電サイクル寿命、信頼性等まだまだ不十分である。

【0003】従来、この種の二次電池の正極を構成する正極活物質としては、充放電反応の形態に依り下記の3種のタイプのものが見い出されている。第1のタイプは、 TiS_2 、 MoS_2 、 $NbSe_3$ 等の金属カルコゲン化合物や、 MnO_2 、 MoO_3 、 V_2O_5 、 Li_xCoO_2 、 Li_xNiO_2 、 $Li_xMn_2O_4$ 等の金属酸化物等々の様に、結晶の層間や格子位置又は格子間隙間にリチウムイオン（カチオン）のみがインターカレーション、デインターカレーション反応等に依り出入りするタイプ。第2のタイプは、ポリアニリン、ポリピロール、ポリパラフェニレン等の導電性高分子の様な、主としてアニオンのみが安定にドーブ、脱ドーブ反応に依り出入りするタイプ。第3のタイプは、グラファイト層間化合物やポリアセン等の導電性高分子等々の様な、リチウムカチオンと

アニオンが共に出入り可能なタイプ（インターカレーション、デインターカレーション又はドーブ、脱ドーブ等）である。

【0004】一方、この種の電池の負極を構成する負極活物質としては、金属リチウムを単独で用いた場合が電極電位が最も早であるため、上記の様な正極活物質を用いた正極と組み合わせた電池としての出力電圧が最も高く、エネルギー密度も高く好ましいが、充放電に伴い負極上にデンドライトや不働体化合物が生成し、充放電による劣化が大きく、サイクル寿命が短いという問題があった。この問題を解決するため、負極として（1）リチウムとAl、Zn、Sn、Pb、Bi、Cd等の他金属との合金、（2） WO_2 、 MoO_2 、 Fe_2O_3 、 TiS_2 等の無機化合物やグラファイト、有機物を焼成して得られる炭素質材料等々の結晶構造中にリチウムイオンを吸蔵させた層間化合物あるいは挿入化合物、（3）リチウムイオンをドーブしたポリアセンやポリアセチレン等の導電性高分子等々のリチウムイオンを吸蔵放出可能な物質を用いることが提案されている。

【0005】

【発明が解決しようとする課題】しかし、一般に、負極活物質として上記の様な金属リチウム以外のリチウムイオンを吸蔵放出可能な物質を用いた負極と、前記の様な正極活物質を用いた正極とを組合せて電池を構成した場合には、これらの物質の電極電位が金属リチウムの電極電位より貴であるため、電池の作動電圧が負極活物質として金属リチウムを単独で用いた場合よりかなり低下するという欠点がある。例えば、リチウムとAl、Zn、Pb、Sn、Bi、Cd等の合金を用いる場合には0.2～0.8V、炭素-リチウム層間化合物では0～1V、 MoO_2 や WO_2 等のリチウムイオン挿入化合物では0.5～1.5V作動電圧が低下する。

【0006】更に、リチウム以外の元素も負極構成要素となるため、体積当たり及び重量当たりの容量及びエネルギー密度が著しく低下する。このため、充放電特性が優れ、サイクル寿命が長く、かつ高電圧、高エネルギー密度の二次電池を得るためには、リチウムに対する電極電位が低く（卑な）、かつ可逆的にリチウムイオンを吸蔵放出できる量の大きい負極活物質が必要である。

【0007】一方、上記の正極活物質に於て、第1のタイプは、一般にエネルギー密度は大きい、過充電や過放電すると結晶の崩壊や不可逆物質の生成等による劣化が大きいという欠点がある。又、第2、第3のタイプでは、逆に容量及びエネルギー密度が小さいという欠点がある。

【0008】このため、過充電特性及び過放電特性が優れ、かつ高容量、高エネルギー密度の二次電池を得るためには過充電過放電に依る結晶の崩壊や不可逆物質の生成が無く、かつ可逆的にリチウムイオンを吸蔵放出できる量のより大きい正極活物質が必要である。

【0009】

【課題を解決するための手段】本発明は、上記の様な問題を解決するため、この種の電池の負極及び／又は正極の電極の活物質として、有機基を有するケイ素と酸素の結合部位を少なくとも1つ以上有する有機ケイ素化合物の熱処理物又は該熱処理物にリチウムを吸蔵させたものから成る新規なリチウムイオン吸蔵放出可能物質を用いることを提起するものである。

【0010】本発明電池の負極及び／又は正極の活物質として用いられる有機ケイ素化合物の熱処理物は次のようにして製造することが出来る。原料の有機ケイ素化合物としては、有機基を側鎖として持つケイ素と酸素の結合部位を少なくとも1つ以上持つ化合物であればよい。中でも、有機基を持つケイ素と酸素が交互に結合してできた主鎖からなるポリマーであるシリコンオイルやシリコンゴム、あるいはシリコン樹脂等が好ましい。これらの化合物は総称して、ポリオルガノシロキサンと言われる。ケイ素に結合した有機基は、炭化水素基、アルコキシ基、 $-N-R_1R_2$ (R_1, R_2 はアルキル基、アリル基、フェニル基、水素等)で示されるアンモニウム基等であれば良く、炭素に結合している一部又は全部の水素が塩素、臭素、ヨウ素等のハロゲン原子に置換されていても良い。中でも有機基としては、メチル基 ($-CH_3$)、エチル基 ($-C_2H_5$)、フェニル基 ($-C_6H_5$)、メトキシ基 ($-OCH_3$)、エトキシ基 ($-OC_2H_5$) 等が好ましい。

【0011】これらの有機ケイ素化合物を200～1000℃の範囲の適当な温度で加熱処理する事により、部分的に縮重合反応あるいは分解が起き、3次元網目構造の化合物が生成する。特に大気中での熱処理の場合には、200℃～600℃、真空中または不活性雰囲気中での熱処理の場合には300℃～1000℃が好ましい。最適な熱処理温度は、原料化合物の分子量、分子構造さらに架橋状態、あるいはケイ素、炭素、酸素等の元素の原料分子中に含まれる割合の違い、等により異なる。

【0012】又、この熱処理物へのリチウムの吸蔵は、次の様に行うことが出来る。即ち、(1) 該熱処理物又は該熱処理物と導電剤及び結着剤等との混合合剤を所定形状に成形したものを一方の電極(作用極)とし、リチウム金属又はリチウムを含有する物質をもう一方の電極(対極)として、リチウムイオン導電性の非水電解質に接して両電極を対向させて電解セルを構成し、作用極がカソード反応をする方向に適当な電流で通電し電気化学的にリチウムイオンを吸蔵させる方法。

【0013】(2) 該熱処理物又は該熱処理物と導電剤及び結着剤等との混合合剤を所定形状に成形し、これにリチウム金属もしくはリチウムの合金等を圧着あるいは接触させて積層電極としたものを電極として電池に組み込む。電池内でこの積層電極が電解質に触れることにより自己放電し電気化学的にリチウムが吸蔵される方

法。

【0014】(3) 該熱処理物を一方の電極の活物質とし、もう一方の電極にリチウムを含有しリチウムイオンを吸蔵放出可能な活物質を用いた電池を構成する。電池として使用中に充放電を行うことにより該熱処理物にリチウムが吸蔵される方法。この様にして得られる熱処理物または該熱処理物にリチウムを吸蔵させたものを負極及び／または正極の活物質として用いる。

【0015】本発明に依る有機ケイ素化合物の熱処理物または該熱処理物にリチウムを吸蔵させたものを活物質とする電極は、これを正負両極に用いて二次電池を構成することが出来るし、又、これを正極または負極の何れか一方の電極として用い、前述のリチウムもしくはリチウムイオンを吸蔵放出可能な各種の他の負極活物質又は正極活物質を用いた電極をもう一方の電極として組み合わせることもできる。特に、本発明の有機ケイ素化合物の熱処理物または該熱処理物にリチウムを吸蔵させたものを活物質とする電極は、金属リチウムに対する電極電位が1V以下の単な領域の充放電容量が大きいことから、これを負極として用い、前述の金属酸化物や金属カルコゲン化合物等々の様な金属リチウムに対する電極電位が2V以上の高電位の活物質を用いた正極と組み合わせることにより高電圧高エネルギー密度でかつ大電流充放電特性に優れ、過充電過放電による劣化の小さい二次電池が得られるので、特に好ましい。

【0016】一方、電解質としては、 γ -ブチロラクトン、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、1,2-ジメトキシエタン、テトラヒドロフラン、ジオキサラン、ジメチルフォルムアミド等の有機溶媒の単独又は混合溶媒に支持電解質として $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiCF_3SO_3$ 等のリチウムイオン解離性塩を溶解した有機電解液、ポリエチレンオキシドやポリフォスファゼン架橋体等の高分子に前記リチウム塩を固溶させた高分子固体電解質あるいは Li_3N , LiI 等の無機固体電解質等のリチウムイオン導電性の非水電解質であれば良い。

【0017】

【作用】本発明の有機ケイ素化合物の熱処理物または該熱処理物にリチウムを吸蔵させたものを活物質とする電極は、非水電解質中に於て金属リチウムに対し少なくとも0～3Vの電極電位の範囲で安定に繰り返しリチウムイオンを吸蔵放出(インターカレーション、デインターカレーションまたはドーピング、脱ドーピング等)することが出来る、この様な電極反応により繰り返し充放電可能な二次電池の負極及び／または正極として用いることが出来る。特にリチウム基準極(リチウム金属)に対し0～1Vの単な電位領域において、安定にリチウムイオンを吸蔵放出し繰り返し充放電できる高容量領域を有する。

【0018】又、従来この種の電池の電極として用いら

れてきたグラファイト等の炭素質材料に比べ可逆的にリチウムイオンを吸蔵放出できる量即ち充放電容量が著しく大きく、かつ充放電の分極が小さいため、大電流での充放電が可能であり、更に過充電過放電による分解等を原因とする劣化が殆ど見られず、極めて安定でサイクル寿命の長い電池を得ることが出来る。

【0019】この様に優れた充放電特性が得られる理由は必ずしも明らかではないが、本発明による新規な活物質である有機ケイ素化合物の熱処理物は、ケイ素と酸素の結合を主鎖とする網状構造又は3次元網目構造の高分子化合物であり、この構造中でのリチウムイオンの移動度が高く、且つ、リチウムイオンを吸蔵できるサイトが非常に多いためリチウムイオンの吸蔵放出が容易である為と推定される。

【0020】

【実施例】以下に、この発明の実施例を図に基づいて説明する。図1は、本発明に依る非水電解質二次電池の電極活物質の性能評価に用いたテストセルの一例を示すコイン型電池の断面図である。

【0021】図1において、1は対極端子を兼ねる対極ケースであり、外側片面をNiメッキしたステンレス鋼製の板を絞り加工したものである。2はステンレス鋼製のネットから成る対極集電体であり対極ケース1にスポット溶接されている。対極3は、所定厚みのアルミニウム板を直径15mmに打ち抜き、対極集電体2に固着し、その上に所定厚みのリチウムフォイルを直径14mmに打ち抜いたものを圧着したものである。7は外側片面をNiメッキしたステンレス鋼製の作用極ケースであり、作用極端子を兼ねている。

【0022】5は後述の本発明に依る活物質又は従来法に依る比較活物質を用いて構成された作用極であり、ステンレス鋼製のネットからなる作用極集電体6と一体に加圧成形されている。4はポリプロピレンの多孔質フィルムからなるセパレータであり、電解液が含浸されている。8はポリプロピレンを主体とするガスケットであり、対極ケース1と作用極ケース7の間に介在し、対極と作用極との間の電気的絶縁性を保つと同時に、作用極ケース開口縁が内側に折り曲げられカシメられることに依って、電池内容物を密封、封止している。電解質はプロピレンカーボネートと1, 2-ジメトキシエタンの体積比1:1混合溶媒に過塩素酸リチウム LiClO_4 を1モル/l溶解したものをを用いた。電池の大きさは、外径20mm、厚さ1.6mmであった。

【0023】以下に活物質の作製例を示す。

(作製例1) 作用極5は次の様にして作製した。有機ケイ素化合物であるポリメチルフェニルシロキサン(PMPS)をキシレンで希釈した溶液(東芝シリコン社製シリコンワニスTSR117)を大気中100°Cで10時間溶媒を揮発させるために加熱乾燥した。次に、この乾燥物を大気中200°Cで5時間熱処理した。冷却

後、粒径 $5.3\mu\text{m}$ 以下に粉碎整粒した。得られた熱処理物を本発明に依る活物質1とし、これに導電剤としてグラファイトを、結着剤として架橋型アクリル酸樹脂等を重量比30:65:5の割合で混合して作用極合剤とし、次にこの作用極合剤をステンレス鋼製のネットからなる作用極集電体6と共に2ton/cm²で直径15mm厚さ0.5mmのペレットに加圧成形した後、100°Cで10時間減圧加熱乾燥したものを作用極とした。この作用極を用いて、前述の構成の電池とした。

【0024】この様にして作製された電池は、室温で1週間放置エージングされた後、後述の充放電試験が行われた。このエージングによって、対極のリチウム-アルミニウム積層電極は電池内で非水電解液に触れることにより十分合金化が進行し、リチウムフォイルは実質的に全てLi-Al合金となるため、電池電圧は、対極として金属リチウムを単独で用いた場合に比べて約0.4V低下した値となって安定した。

【0025】以上の様に作製した電池を、0.4mAの定電流で、充電(作用極にリチウムイオンが吸蔵される電池反応をする電流方向)の終止電圧-0.4V、放電(作用極からリチウムイオンが放出される電池反応をする電流方向)の終止電圧2.5Vの条件で充放電サイクルを行ったときの3サイクル目の充電特性を図2に、放電特性を図3、1~5サイクルのサイクル特性を図4に示した。また、-0.8V~2.5Vの電圧範囲での3サイクル目の充電特性を図5に、放電特性を図6に、1~5サイクルのサイクル特性を図7に示した。尚、充放電サイクルは充電からスタートした。

【0026】(作製例2) 前述のPMPS乾燥物の熱処理を大気中300°Cで10時間とした以外は作製例1と同様の方法で活物質2を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図2、図3、図4に、また、-0.8V~2.5Vの電圧範囲での充電特性を図5に、放電特性を図6に、サイクル特性を図7に示した。

【0027】(作製例3) 前述のPMPS乾燥物の熱処理を大気中400°Cで10時間とした以外は作製例1と同様の方法で活物質3を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図2、図3、図4に、また、-0.8V~2.5Vの電圧範囲での充放電特性を図5、図6、図7に示した。-0.8V~2.5Vの充放電を10サイクル行った後に充電状態及び放電状態のそれぞれの電池を分解観察したところ、作用極側へリチウムが析出している様子もなく、また電解質の分解等によるガス発生も極少量であり、作用極の充放電反応は実質的に活物質へのリチウムイオンの吸蔵放出であることが確認された。

【0028】(作製例4) 前述のPMPS乾燥物の熱処

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理を大気中500℃で10時間とした以外は作製例1と同様の方法で活物質4を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図2、図3、図4に、また-0.8V~2.5Vの電圧範囲での充放電特性を図5、図6、図7に示した。

【0029】(作製例5) 前述のPMP S乾燥物の熱処理を大気中600℃で10時間とした以外は作製例1と同様の方法で活物質5を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図2、図3、図4に、また-0.8V~2.5Vの電圧範囲での充放電特性を図5、図6、図7に示した。

【0030】(作製例6) 前述のPMP S乾燥物の熱処理を窒素雰囲気中500℃で5時間とした以外は作製例1と同様の方法で活物質6を作製し、同様な電池を作製した。作製例1と同様な方法で、-0.4V~2.5Vの充放電特性の測定を行い、その充電特性を図8に、放電特性を図9に、サイクル特性を図10に示した。

【0031】(作製例7) 前述のPMP S乾燥物の熱処理を窒素雰囲気中700℃で5時間とした以外は作製例1と同様の方法で活物質7を作製し、同様な電池を作製した。作製例1と同様な方法で、-0.4V~2.5Vの電圧範囲での充放電特性の測定を行い、その結果を図8、図9、図10に示した。

【0032】(作製例8) 前述のPMP S乾燥物の熱処理を窒素雰囲気中800℃で12時間とした以外は作製例1と同様の方法で活物質8を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図8、図9、図10に示した。また、-0.8V~2.5Vの電圧範囲での充電特性を図11に、放電特性を図12に、サイクル特性を図13に示した。

【0033】(作製例9) 前述のPMP S乾燥物の熱処理を窒素雰囲気中1000℃で12時間とした以外は作製例1と同様の方法で活物質9を作製し、同様な電池を作製した。作製例1と同様な方法で充放電特性の測定を行い、-0.4V~2.5Vの電圧範囲での充放電特性を図8、図9、図10に、また-0.8V~2.5Vの電圧範囲での充放電特性を図11、図12、図13に示した。

【0034】(比較例1) 比較のために、作製例1における活物質1の代わりに、導電剤として用いているグラファイトと同じグラファイトを活物質として用いた以外は作製例1と同様の方法で電池を作製した。作製例1と同様に-0.4V~2.5Vの電圧範囲での充放電特性を測定し、その結果を図2、図3、図4に示す。

【0035】(比較例2) 比較のために、作製例1における活物質1の代わりに二酸化ケイ素SiO₂を活物質として用いた以外は作製例1と同様の方法で電池を作製

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した。作製例1と同様に-0.4V~2.5Vの電圧範囲での充放電特性を測定し、その結果を図2、図3、図4に示す。

【0036】図2~13から明らかな様に、本発明による有機ケイ素化合物の熱処理物を活物質として用いた電池はいずれも比較例1、2に比べ、充放電容量が著しく大きく、充放電の可逆領域が著しく拡大することが分かる。又、充放電の繰り返しによる放電容量の低下(サイクル劣化)が著しく小さい。更に、全充放電領域に渡って充電と放電の作動電圧の差が著しく小さくなっており、電池の分極(内部抵抗)が著しく小さく、大電流充放電が容易なことが分かる。これは、上述の様に本発明に依る電池の作用極の活物質である有機ケイ素化合物の熱処理物に於いては、ケイ素と酸素及び炭素が共存し、それらの原子が直接相互に結合した網状構造又は3次元網目構造を有することによりリチウムイオンの移動度が高く、かつリチウムイオンを吸蔵できるサイトが多いためと推定される。

【0037】又、本発明に依る活物質を用いた電池はLi-A1合金電極に対して1.0~2.5V(金属リチウムに対して約1.4~2.9Vに対応する)の貴な電位領域と同様、もしくはそれ以上に、-0.4~+0.6V(金属リチウムに対して約0~1Vに対応する)の卑な電位領域の充放電容量が大きいことから、非水電解質二次電池の正極活物質として用いられるのみならず、負極活物質としても優れていることが判る。特に大気中200℃~400℃、不活性雰囲気中700℃以下で熱処理を行った活物質1、2、3、6、7を用いた電池では、卑な電位領域での充放電容量がより大きく、かつより卑な電位を有しており、より負極活物質として優れている。

【0038】尚、実施例においては、対極としてリチウム-アルミニウム合金の場合のみを示したが、本発明は実施例に限定されず、前述の様に、金属リチウム、リチウムとZn, Sn, Pb, Bi等の他金属との合金、炭素やMoO₂, WO₂, Fe₂O₃等のリチウム挿入化合物、ポリアセチレン、ポリピロール、ポリアセン等のリチウムイオンをドーピング可能な導電性高分子等々のリチウムを吸蔵放出可能な物質を活物質とする負極や、TiS₂, MoS₂, NbSe₃等の金属カルコゲン化合物、MnO₂, MoO₃, V₂O₅, Li_xCoO₂, Li_xNiO₂, Li_xMn₂O₄等の金属酸化物、ポリアニリン、ポリピロール、ポリパラフェニレン、ポリアセン等の導電性高分子、グラファイト層間化合物等々の様なリチウムカチオン及び/またはアニオンを吸蔵放出可能な物質を活物質とする正極を対極として本発明に依る電極と組合わせて用いることが出来ることは言うまでもない。

【0039】

【発明の効果】以上の様に、本発明は、非水電解質二次電池の負極及び/又は正極の電極の活物質として、有機

基を有するケイ素と酸素の結合部位を少なくとも1つ以上有する有機ケイ素化合物の熱処理物又は該熱処理物にリチウムを吸蔵させたものから成る新規な活物質を用いたものであり、充放電により可逆的にリチウムイオンを吸蔵放出できる量即ち充放電容量が著しく大きく、かつ充放電の分極が小さいため、大電流での充放電が可能であり、更に過充電過放電による分解や結晶崩壊等の劣化が殆ど見られず、極めて安定でサイクル寿命の長い電池を得ることが出来る。又、特に、本発明による該活物質を負極活物質として用いた場合には、高電圧かつ高エネルギー密度の電池を得ることが出来る等々優れた効果を有する。

【図面の簡単な説明】

【図1】本発明において実施した電池の構造の一例を示した説明図である。

【図2】本発明による活物質1、活物質2、活物質3、活物質4、活物質5を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vの充電特性の比較を示した説明図である。

【図3】本発明による活物質1、活物質2、活物質3、活物質4、活物質5を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vの放電特性の比較を示した説明図である。

【図4】本発明による活物質1、活物質2、活物質3、活物質4、活物質5を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vのサイクル特性の比較を示した説明図である。

【図5】本発明による活物質2、活物質3、活物質4、活物質5を用いた電池の-0.8V~2.5Vの充電特性を示した説明図である。

【図6】本発明による活物質2、活物質3、活物質4、活物質5を用いた電池の-0.8V~2.5Vの放電特性を示した説明図である。

【図7】本発明による活物質2、活物質3、活物質4、活物質5を用いた電池の-0.8V~2.5Vのサイクル特性を示した説明図である。

【図8】本発明による活物質6、活物質7、活物質8、活物質9を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vの充電特性の比較を示した説明図である。

【図9】本発明による活物質6、活物質7、活物質8、活物質9を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vの放電特性の比較を示した説明図である。

【図10】本発明による活物質6、活物質7、活物質8、活物質9を用いた電池と、比較例1、比較例2による電池の-0.4V~2.5Vのサイクル特性の比較を示した説明図である。

【図11】本発明による活物質8、活物質9を用いた電池の-0.8V~2.5Vの充電特性を示した説明図である。

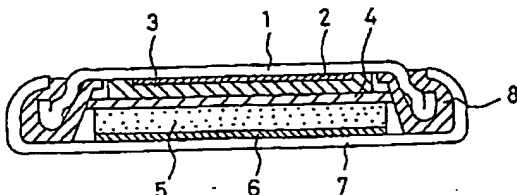
【図12】本発明による活物質8、活物質9を用いた電池の-0.8V~2.5Vの放電特性を示した説明図である。

【図13】本発明による活物質8、活物質9を用いた電池の-0.8V~2.5Vのサイクル特性を示した説明図である。

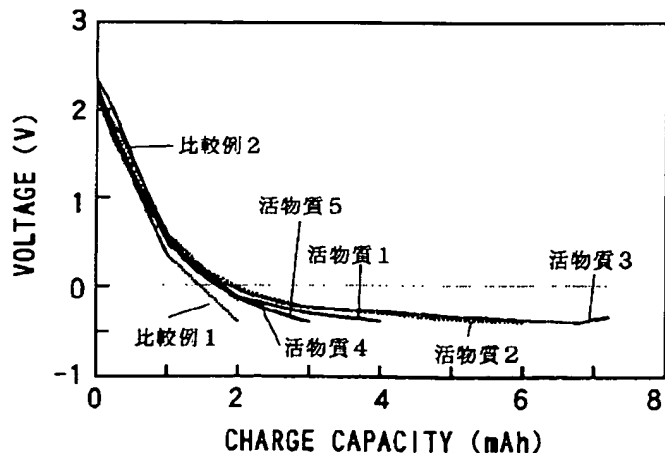
【符号の説明】

- 1 対極ケース
- 2 対極集電体
- 3 対極
- 4 セパレータ
- 5 作用極
- 6 作用極集電体
- 7 作用極ケース
- 8 ガスケット

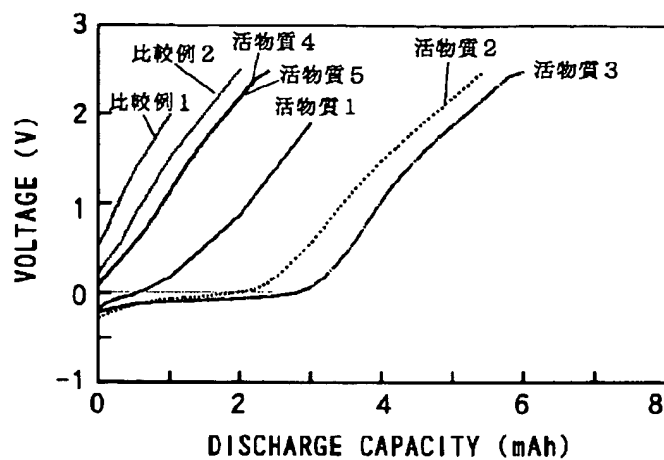
【図1】



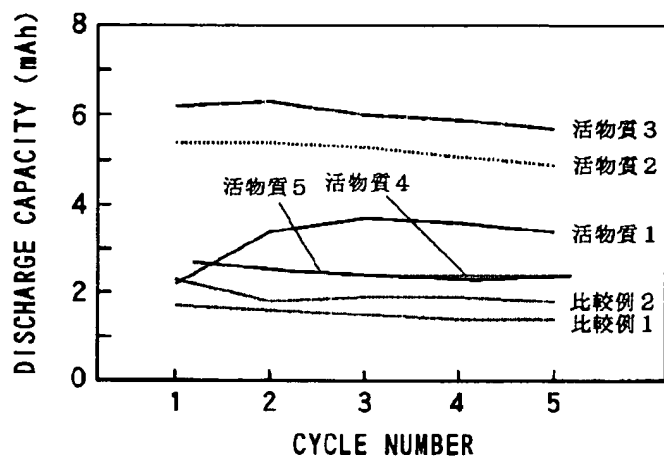
【図2】



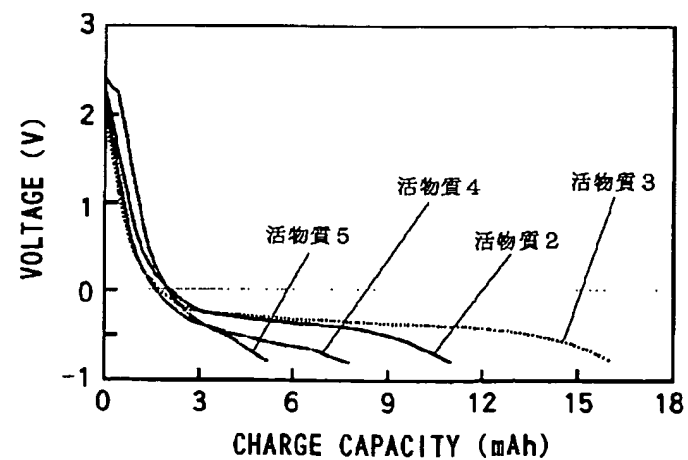
【図3】



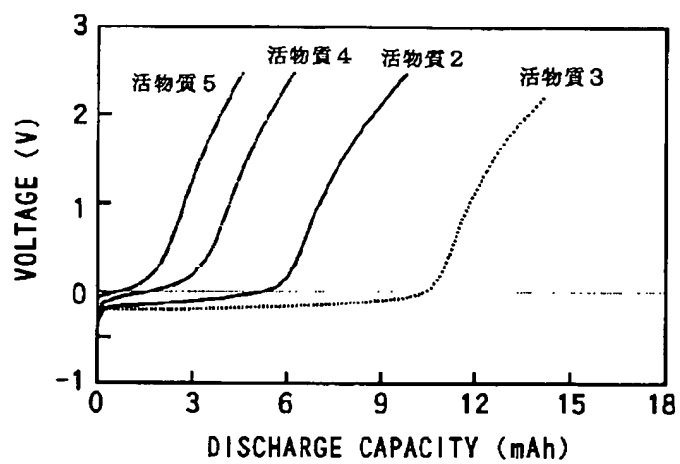
【図4】



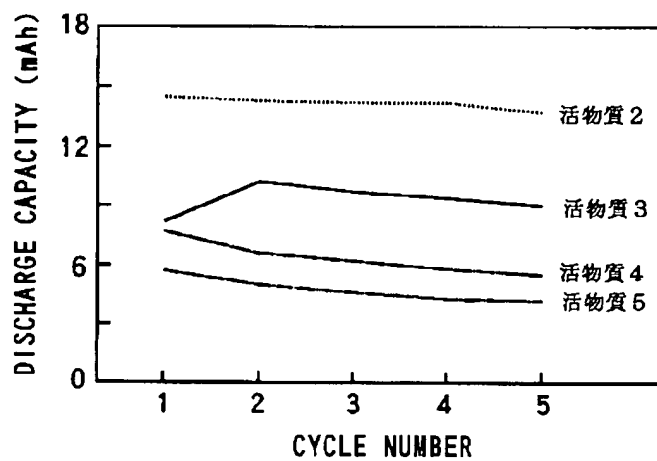
【図5】



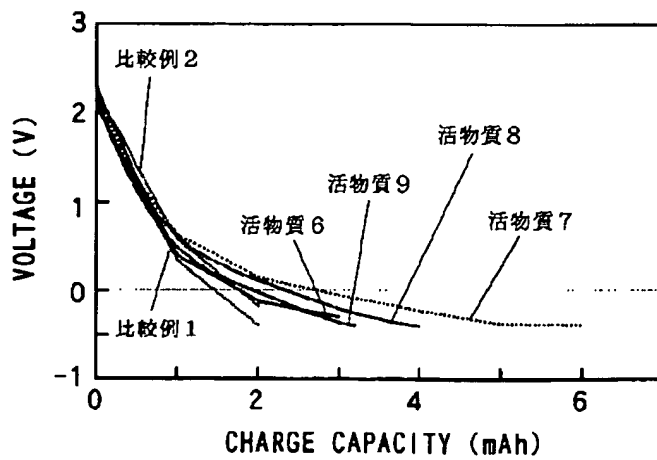
【図6】



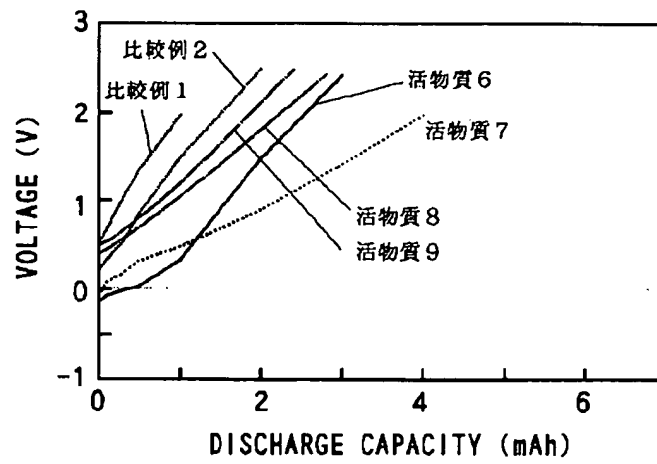
【図7】



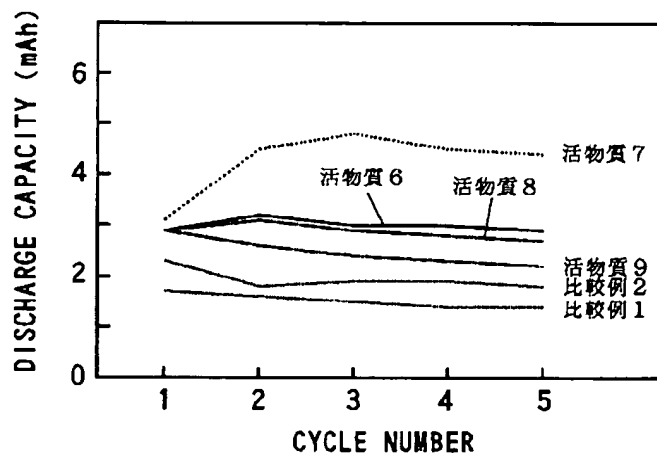
【図8】



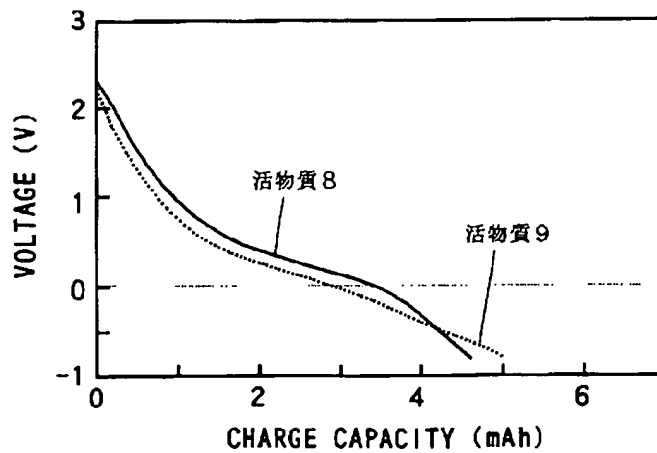
【図9】



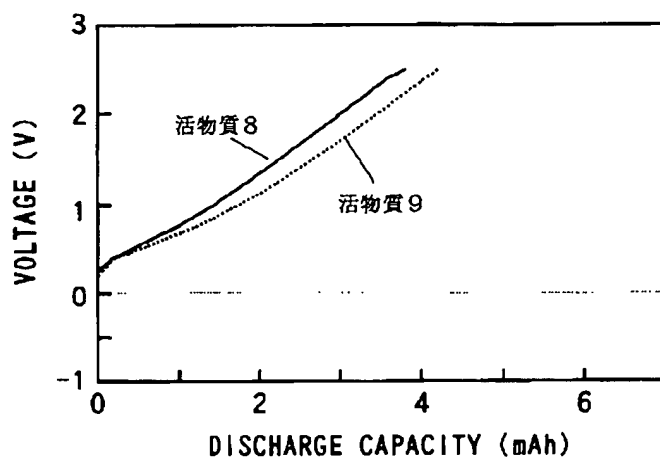
【図10】



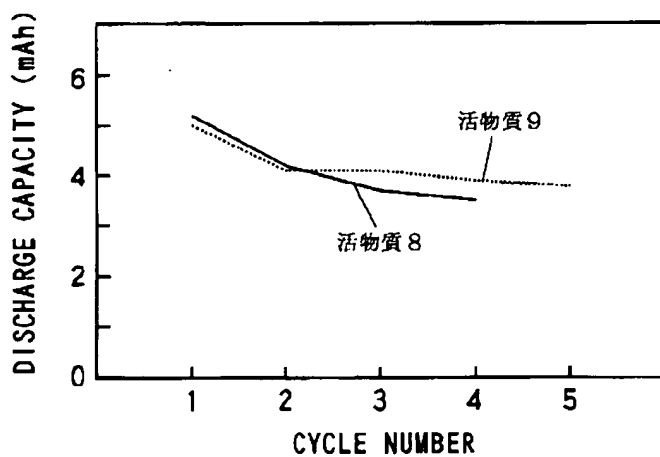
【図11】



【図12】



【図13】



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